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Thermodynamic Studies of Complex Formation Between Co(SALEN) Ionophore with Chromate (II) Ions in AN-H_2O Binary Solutions by The Conductometric Method

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The complexation reaction between CrO_4^{2-} anion with macrocyclic ligand, N,N′Bis(salicylidene) ethylenediamino cobalt(II) (Co(SALEN)), was studied in acetonitrile–water (AN–H_2O) binary mixed systems at 25°C. The conductance data show that the stoichiometry of the complexes formed between (Co(SALEN)) with CrO_4^{2-} anion in most cases is 1:1 [M:L], but in the case of the 89.70% mol AN-H_2O binary solution 1:2 [$M:L_2$] complex is formed in solutions. The values of stability constant ($\log K_f$) of (Co(SALEN)-CrO_4^{2-}) complex at 25°C which was obtained from conductometric data, shows that the nature and also the composition of the solvent systems are important factors that are effective on the stability and even the stoichiometry of the complex formed in solutions. In all cases, a non-linear relationship is observed for the changes of stability constants ($\log K_f$) of the (Co(SALEN)-CrO_4^{2-}) complexes versus the composition of the binary mixed solvents.

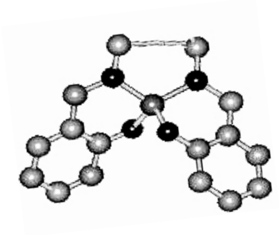
Keywords: N,N′Bis(salicylidene) ethylenediamino cobalt(II), Chromate (II), Acetonitrile–water (AN–H_2O) binary mixed systems, Conductometry.

1. INTRODUCTION

Macrocyclic compounds are polydentate ligands with donor atoms attached to a cyclic backbone. The first macrocyclic compound was reported 100 years ago by Werner, who introduced the concept of coordination chemistry [1]. Later, Lehn introduced the concept of supramolecular chemistry according to molecular assembly and host–guest chemistries [2]. The understanding of the metal–ion chemistry of macrocyclic ligands has important implications for a range of chemical and biochemical areas. Macrocyclic compounds are polydentate ligands containing their donor atoms attached to a cyclic backbone. A search of chemical abstracts shows that most of the publications based on applications of these macrocyclic ligands are related to their complex reactions with different metal cations and with anions. Due to this fact, many researchers have carried out a wide range of applications for these macrocyclic compounds in different areas such as the construction of ISEs [3], separation of metal cations [4], as a stationary phase in chromatography columns [5], designing chemical sensors [6], recognition of isomers [7], and chemical analysis [8]. In the recent years, this branch of chemistry has attained a lot of developments. Many new novel compounds with high selectivities for ion or molecule separation, transport and catalytic purposes have been developed by scientists who are active in different areas of chemistry.

Complexation and selectivity behaviour of an ionophore are evaluated in different ways. One method for evaluating the binding properties of the ionophore according to the ISE response is with a membrane with two ionophores that have been used as the base-membrane. In other methods, the response between two different membranes based on the ionophore-based membrane is sandwiched with an ionophore-free membrane and then compared. All of these methods are evaluated after its incorporation into the sensor [9, 10].

Other methods to examine the selectivity and potential of a would-be ionophore outside of the membrane phase include: the strength of the ion–ionophore interactions in the solution phases via NMR [11], complexation study by conductometric method [12, 13], UV-VIS study [14, 15], and polarographic study [16, 17].



Scheme 1. N,N′Bis(salicylidene) ethylenediamino cobalt(II)

Conductivity measurements can also be useful tools to investigate complexation, as they offer precision, simplicit, and low cost. Here, we discuss the complexation of N,N′Bis(salicylidene) ethylenediamino cobalt(II) (Scheme 1) with chromate (CrO_4^{2-}) anion in water (H_2O), acetonitrile (AN) and their binary mixture solutions at different temperatures using the conductometric method. The goal of the present investigation is to study the effect of solvent properties and the composition of the binary mixed solvents on stoichiometry and the selectivity between ligands and ions in various solvent systems.

2. EXPERIMENTAL PROCEDURE

A Potassium Chromate (HmbG), Co(SALEN) (Merck) were used without further purification. Deionized bi-distilled water was used throughout the experiment. Acetonitrile from Merck also was used with the highest purity. The conductance measurements were performed on a digital Hanna conductivity apparatus (Model HI 255) in a thermostated water bath with a constant temperature maintained within ±0.01°C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.99 cm^{-1} was used throughout the studies. The cell was calibrated with a standard solution of KCl (0.1000 M). In a typical experiment, 25 ml of anion salt solution (potassium chromate (5.0×10^{-4} M)) was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to the thermostated circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same target ion concentration. The conductances of the initial solutions were measured after thermal equilibrium had been reached. A known amounts of the macrocycle solution (2.5×10^{-2}M Co(SALEN)) was then added in a stepwise manner using a calibrated micropipette. The conductances of the solutions were measured after each addition. Addition of the ligand continued until the desired ligand-to-anion mole ratios were achieved. The stability constants of the complexes formed between ligand and this target anion was calculated from the variation of the molar conductance as a function of ligand-to-anions mole ratio using a GENPLOT computer program [18].

3. RESULTS

This research investigates the results of the thermodynamic study and the selectivity for complexation reactions between Co(SALEN) ligand with chromate (CrO_4^{2-}) anions in acetonitrile–water (AN–H_2O) binary mixtures at different temperatures using the conductometric method.

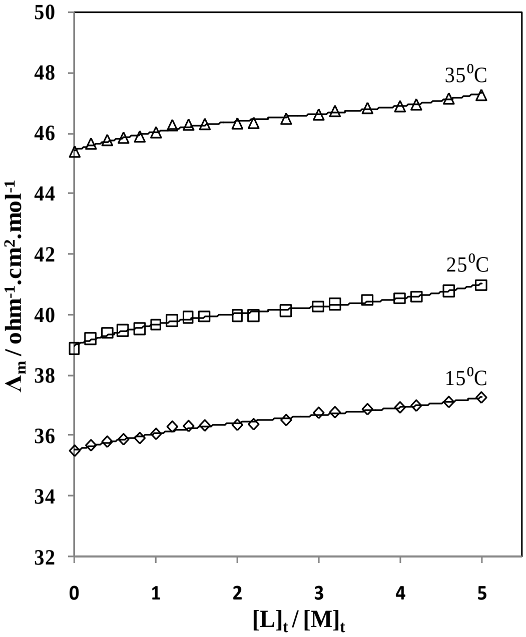


Figure 2. Molar conductance–mole ratio plots for the $(Co(SALEN)\text{-}CrO_4)^{2-}$complex in AN–$H_2O$ binary mixture (mol% H_2O=24.37) at different temperatures.

It also evaluated the effect of the macrocyclic ligand (Co(SALEN)) on the nature of chromate anions and the composition of the acetonitrile–water binary solutions. To the best of our knowledge, this is the first reported thermodynamic study of chromate ions using the conductometric method. The results can be used for many applications of chromate ions such as the fabrication of ISE based on macrocyclic ionophores for determining of chromate ions in real samples.

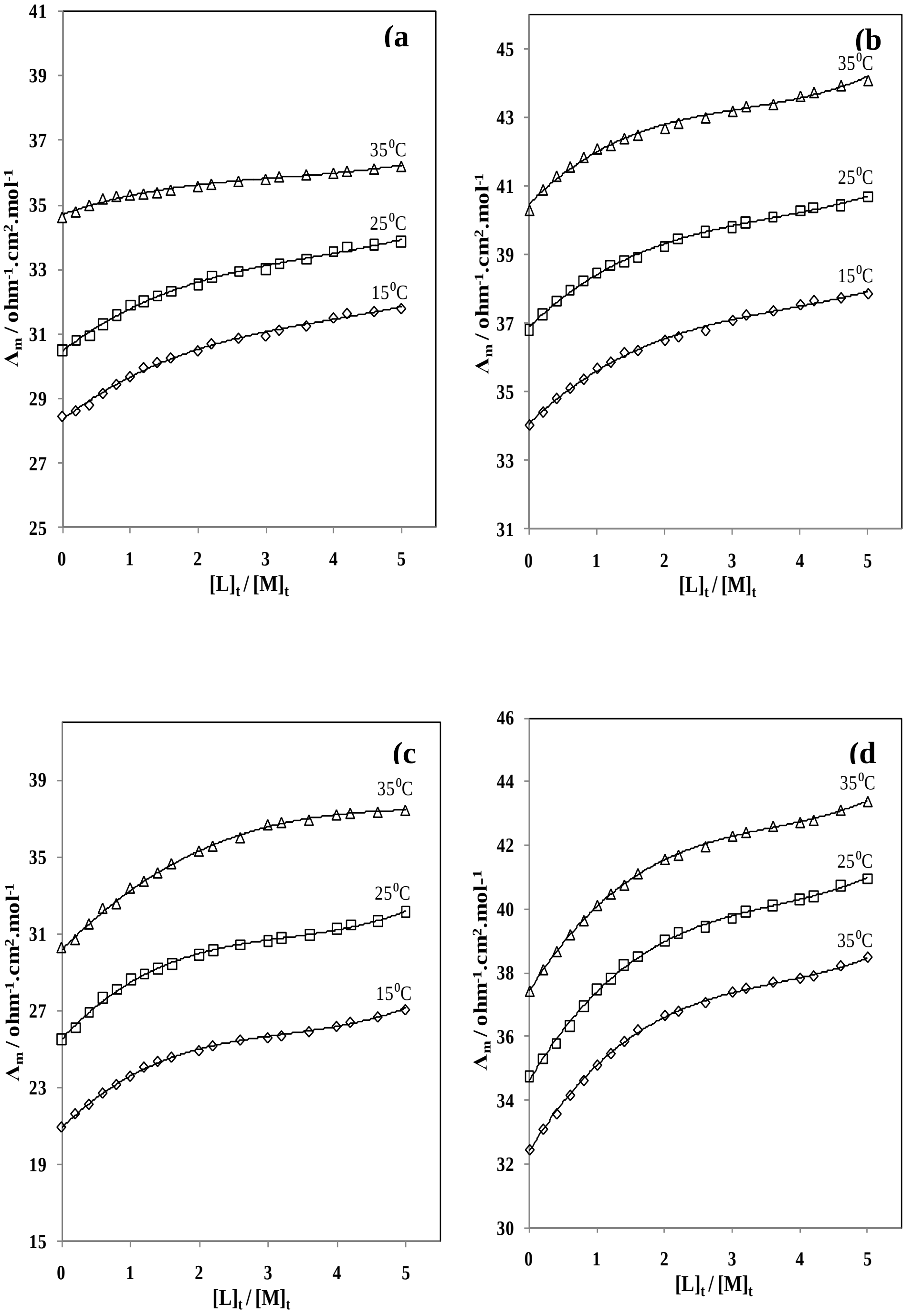


Figure 3. Molar conductance–mole ratio plots for the $(Co(SALEN)\text{-}CrO_4)^{2-}$ complex in AN–H_2O binary mixture (mol% H_2O = (a):49.16, (b):74.36, (c):81.32, (d):89.70) at different temperatures.

Changes in molar conductivity (Λ_m) versus the ligand-to-ion molar ratio, ($[L]_t$ / $[M]_t$) for the complexation of Co(SALEN) with CrO_4^{2-} anion was measured in pure AN and water and in AN–H_2O binary systems at different temperatures. In the study, $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total concentration of the chromate ion. Changes in molar conductivity versus the ligand-to-anion molar ratio, for complexation of Co(SALEN) with CrO_4^{2-} anion were measured in the AN-H_2O binary system at different temperatures. The results are shown in Figures 2 and 3. The ligand and anion salts were insoluble in pure water and acetonitrile solvents, respectively.

Fig shows the molar conductance vs. the [L] / [M] curves for Co(SALEN)-CrO_4^{2-} complexes in AN-H_2O (mol% H_2O=24.37) at different temperatures. The plots (in Fig) exhibit one obvious slope, suggesting that the probable stoichiometry ratio of complexes are M:L. Incidentally, as expected, the corresponding molar conductance increased with the increase in temperature due to the decreased viscosity of the solvent and, consequently, the enhanced mobility of the charged species present in the solution.

As seen in Figure (a, b, c, d), in three AN-H_2O binary systems (mol% H_2O = (a):49.16, (b):74.36 and (c):81.32), the slope of the corresponding molar conductance versus ligand-to-anion mole ratio is about one. However, in one composition of this binary mixed solvent (mol% H_2O = 89.70), the slope of each curve changes at the point where $[L]_t$ / $[M]_t$ is about two, which suggests the formation of a 1:2 [ML_2] complex between the Co(SALEN) and CrO_4^{2-} anion in these solutions (Figured).

The results obtained in this investigation indicate that the property and the composition of the solvent system are significant factors affecting the stoichiometry and stability of the complexes formed between the Co(SALEN) and CrO_4^{2-} anion in AN-H_2O binary solutions [19].

The main goal of the conductometric study was to obtain the stability constant complexes between ligands and ions.

Table 1. Log K_f values of Co(SALEN)-CrO_4^{2-} complexes in AN–H_2O binary mixtures at different temperatures.

Medium	Log K_f ± SD[a]		
Pure AN	c	c	c
75.63% AN-24.37% H_2O	2.56 ± 0.10	2.58 ± 0.19	2.58 ± 0.08
50.84% AN-49.16% H_2O	2.96 ± 0.05	2.97 ± 0.05	2.98 ± 0.10
25.64% AN-74.36% H_2O	3.06 ± 0.04	3.08 ± 0.17	3.10 ± 0.08
18.68% AN-81.32% H_2O	3.20 ± 0.06	3.26 ± 0.06	3.17 ± 0.04
10.30% AN-89.70% H_2O	3.24 ± 0.03	3.21 ± 0.04	3.25 ± 0.03
Pure H_2O	c	c	c

[a] SD = Standard deviation.

[b] The composition of each solvent system is expressed in mole% of each solvent.

[c] Ion or ligand salt is insoluble.

Table presents log K_f values of complexes formed at different temperatures between Co(SALEN) with the CrO_4^{2-} anion in pure AN, in pure H_2O, and in their binary mixtures.

4. DISCUSSION

The complexation reaction between a target ion (cation or anion) with a ligand in a solution which is an equilibrium process can be considered as

$$(\text{ion}^{n\pm})\,S_x + (\text{ligan})\,S_y = (\text{ion} - \text{ligand})^{n\pm}\,S_z + (x + y - z)\,S \qquad \text{(Equation 1)}$$

where S is the solvent molecule, and x, y and z are the solvation numbers of the ions, the ligand, and the resulting complex, respectively.

According to Equation 1, the affinity of the ligand and solvent for the metal cation or anion and the affinity of the target ion or the solvent molecules for the ligand result in the change of free energy. Therefore, the solvation of the target ion, ligand, and resulting complex influence the complex formation constant, the Gibbs energy of the complexation process, and its enthalpy in the solutions [20]. These effectives express by the Gutman donor number [21].

Indeed, when the donor number of the solvent is low, the ion is poorly solvated and can easily be copmlexed by the ligand, which results in the formation of a strong complex in solution. Instead, in a strong solvating solvent such as dimethylsulfoxide (DMSO) with a relatively high Gutman Donor Number (DN = 29.8), the solvation of the target ions and possibly of the ligand should be stronger than those of solvents with less solvating ability such as acetonitrile (AN).

From Table , it is obvious that the nature of the solvent has a fundamental effect on the stability of the resulting complexes. In most cases, the stability constant of the complexes increases with the temperature in most solvent systems, which is evidence for an endothermic complexation reaction between ligands and ions in the solutions. The stability constant of $(Co(SALEN)\text{-}CrO_4)^{2-}$ complex increases with the increase in the mol% of water in the AN-H_2O binary solvent system. This is in contrast with the Gutman donor number principle. However, the theory of soft acid and soft base can explain this observation. According to this theory, since the Co(SALEN) ligand is a soft acid, it is strongly solvated by acetonitrile molecules, because its nitrogen atom acts as a soft base [22]. Therefore, by increasing the mol% acetonitrile in mixtures, the values of log K_f decreases as shown in Table .

The Gibbs energy $\Delta_f G^o$, and entropy $T\Delta_f S^o$ of the complex formation, are calculated from the known thermodynamic relations [23]:

$$\Delta_f G^o = -RT \ln K_f = \Delta_f H^o - T\Delta_f S^o \qquad \text{(Equation 2)}$$

The calculated thermodynamic parameters ($\Delta H_c^o, \Delta G_c^o, \Delta S_c^o$) at 25°C for Co(SALEN)-$CrO_4^{2-}$ complexes in pure AN, pure H_2O, and AN-H_2O binary systems are listed in Table . The experimental values of standard enthalpy (ΔH_c^o) and standard entropy (ΔS_c^o) given in Table show that, in most cases, the complexes are enthalpy destabilized but entropy stabilized. Therefore, the entropy of the complexation reactions is the principal driving force for the formation of this complex in most solvent systems.

The experimental results show that in all cases, the change in standard enthalpy for the complexation reaction between ligand and ion is negligible; therefore, it seems that the complexation processes in most of the solvent systems are probably athermic.

Table 2. Thermodynamic parameters for Co(SALEN)-CrO_4^{2-} complex in AN–H_2O binary mixtures.

Medium	$-\Delta G_c^o \pm \mathrm{SD}^a$	$\Delta H_c^o \pm \mathrm{SD}^a$	$\Delta S_c^o \pm \mathrm{SD}^a$
	kJ/mol	kJ/mol	J/mol.°K
75.63% AN-24.37% H_2O	14.71±1.80	2.00±0.51	56.06±3.19
50.84% AN-49.16% H_2O	16.93±0.32	1.94±0.21	63.33±0.81
25.64% AN-74.36% H_2O	17.57±1.00	3.62±0.06	71.09±3.37
18.68% AN-81.32% H_2O	18.30±0.37	7.40±0.93	87.21±2.90
10.30% AN-89.70% H_2O	18.35±0.23	2.96±0.94	71.49±3.05

[a] SD = Standard deviation.

[b] The composition of each solvent system is expressed in mole% of each solvent.

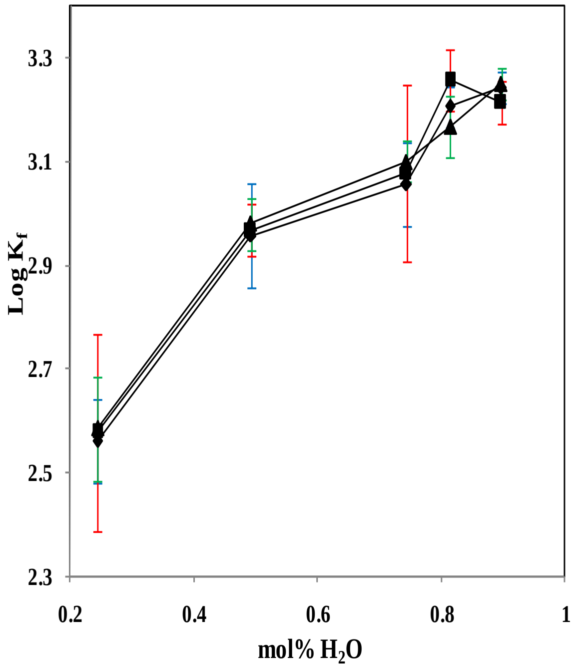


Figure 4. Changes of the stability constant (log K_f) of $(Co(SALEN)\text{-}CrO_4)^{2-}$ complex with the composition of AN–H_2O binary systems at different temperatures: (♦15°C, ■ 25°C, ▲ 35°C).

As shown in Fig 4., changes in the stability constant (log K_f) of the $(Co(SALEN)\text{-}CrO_4)^{2-}$ complex versus the composition of the AN–H_2O binary system at various temperatures are not linear.

This behaviour is probably due solvent–solvent interactions that changed the structure of the solvent mixtures and therefore changed the solvation properties of the chromate anion, the Co(SALEN), and the resulting complex. In addition, the preferential solvation of the anion and ligand as well as the characteristics of its changes with the composition of the mixed solvents and temperature may be another reason for this kind of behaviour [13]. The interactions between some binary mixed solvents have been studied. For example, mixing dimethylformamide with acetonitrile induces the mutual destruction of the dipolar structures of these dipolar aprotic liquids and releases the free dipoles [24]. As a result, strong dipolar interaction between acetonitrile and water molecules is expected.

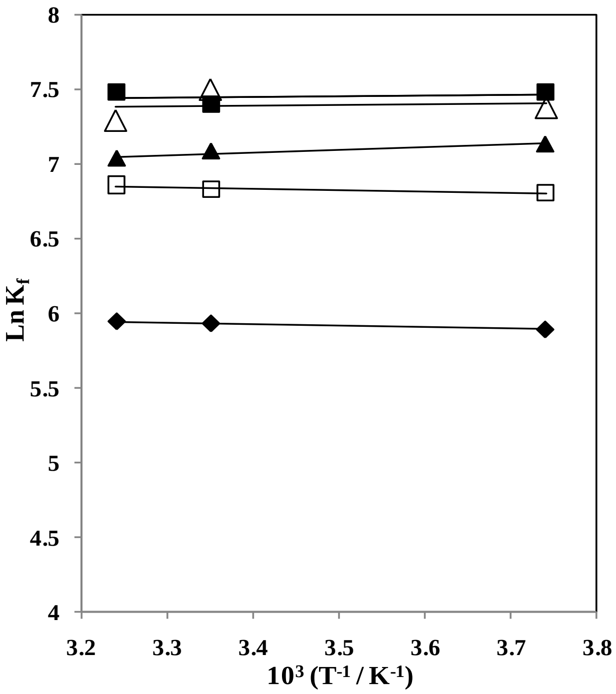


Figure 5. Van’t Hoff plots for $(Co(SALEN)\text{-}CrO_4)^{2-}$ complex in AN–H_20 binary systems: (mol% AN: ♦ 75.63, □ 50.84, ▲ 25.64, Δ 18.68, ■ 10.30).

The Van’t Hoff plots of $\ln K_f$ versus 1/T for all of the investigated systems are provided. A typical example of this plot for $(Co(SALEN)\text{-}CrO_4)^{2-}$ complexes in pure AN, pure H_2O and AN-H_2O binary systems is shown in Fig. 5. According to Equation 2, The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively; the results are also included in Table [25].

5. CONCLUSIONS

The stability constant for the complexation of $Co(SALEN)_2$ with chromate anion in acetonitrile-water (mole%) binary solvents was determined conductometrically at different temperatures. According to the obtained results, compression of the formation constant (at identical temperature) shows that in the case of Co(SALEN)$_2$-CrO$_4^{2-}$ complex, the stability constant of the complex increased with the increasing water percentage. The negative value of ΔG^o proves the ability of the ligand to form stable complexes and of the process trend to proceed spontaneously. Furthermore, the positive values of ΔS^o indicate that entropy is responsible for the complexing process in other systems. Moreover, Co(SALEN)$_2$ form a 1:1 complex with the CrO$_4^{2-}$ anion in all compositions of the AN-H$_2$O binary solution. In the case of the 89.70% mol AN-H$_2$O binary solution, a 1:2 complex formed. Hence, the results show that it is possible to change in the stabilities, selectivities, and stoichiometry of complexes that form between macrocyclic ligands and ions with the composition of the mixed solvent systems. The average stability constants (log K$_f$) for the Co(SALEN)$_2$-CrO$_4^{2-}$ complexes at 25 ^{o}C was 3.02. These results show that the mentioned macrocyclic ligands can be used to determine chromate ions. Accordingly, this ligand can be used as a sensing element in the membrane to fabricate the ion selective electrode.

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